We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Fluorescent Markers in Water Treatment

Maxim Oshchepkov and Konstantin Popov

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.76218>

Abstract

Both phosphonate- and polymer-based scale inhibitors have a broad spectrum of applications in water treatment technologies. However, the “online” monitoring of antiscalant content in an aqueous phase is still a challenge for researchers. A possible solution is provided by the fluorescent markers added to the feeding water. These can be either an antiscalant tagged or may represent the independent species. The review summarizes both the advantages and the drawbacks of these approaches along with such markers’ classification, with a special emphasis on the novel fluorescent-tagged phosphonates. Besides, some unique opportunities provided by the fluorescent-tagged antiscalants for reverse osmosis membrane mapping, scale inhibition traceability, and a scale inhibitor localization in a circulation water facility are also considered and discussed.

Keywords: scale inhibition, fluorescent markers, water treatment

1. Introduction

Fluorescence is the emission of light by a substance that has absorbed light with a different wavelength or electromagnetic radiation. It has many practical and valuable applications, including in mineralogy, gemology, medicine, chemical sensors (fluorescence spectroscopy), fluorescent labeling, dyes, biological detectors, environmental monitoring, cosmic-ray detection, and, most commonly, fluorescent lamps [1–5]. However, in the field of water treatment, it has gained increasing interest mostly in the last decade [6–8]. The water treatment technologies use fluorescence phenomenon for the oil component control in wastewater [9], gaseous oxygen monitoring in wastewater [10], water leaks in industrial pipelines [11], for the total bacterial count [12], and for online scale inhibitors’ content monitoring [6–8, 13]. Besides, the problem of a scale inhibition mechanism is still actual and requires applications of fluorescent-tagged inhibitors [14]. All these applications are to be considered in a recent review.

2. Fluorescent monitoring of a scale inhibitor content

Scale formation in the upstream oil and gas industry, reverse osmosis desalination processes, steam generators, boilers, cooling water towers, and pipes is a serious problem, causing significant plugging of wells, pipelines, membranes, and increasing the production cost [15]. A widely used technique for controlling scale deposition is an application of chemical inhibitors [16, 17]. Commonly used commercial antiscalants are represented by chemical families: polyphosphates (hexametaphosphate (HMP), tripolyphosphate (TPP), etc.), organophosphonates (aminotris(methylenephosphonic acid), ATMP; 1-hydroxyethane-1,1-bis(phosphonic acid), HEDP; 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC); ethylenediaminetetra(methylenephosphonic acid), EDTPH, etc), and organic polyelectrolytes (polyacrylates (PA), polycarboxysulfonates, (PCS)). Among these, the organophosphonates are dominating the world market at present. At the same time, phosphorus-based inhibitors are hardly biodegradable and persist for many years after their disposal, which lead to eutrophication problems. Phosphorus discharges are therefore regulated in many countries worldwide, and permissible limits are constantly decreasing [18].

Increasing environmental concerns and discharge limitations have forced the scale-inhibitor chemistry to move toward “green antiscalants,” that are readily biodegradable and have minimal environmental impact [17, 18]. Intensive efforts have been applied recently to develop the “green” alternatives to organophosphonates and nonbiodegradable polyacrylates. Among these novel inhibitors, such chemicals as polymaleates (PMAs), polyaspartates (PASPs), polyepoxysuccinates (PESAs), as well as their various derivatives, including co-polymers with PA, are worth mentioning [19, 20].

The concentration of polymeric antiscalants in the circulating system is usually changed by evaporation of water, reagent sorption on the pipe surfaces, and by a periodical discharge of the circulating water with some deposit. Therefore, an adequate monitoring of the polymer concentration is needed to minimize the consumptions of both scale inhibitor and water. Along with conventional monitoring methods based on UV-vis or potentiometry, the intensity of fluorescence emitted from either indifferent markers or a covalently bound to polymer tracer becomes a matter of choice [6].

The conventional monitoring methods for PA and for other polymeric antiscalants are classified into four groups [21]: (i) monitoring a spectral change caused by the interaction of PA with some metal-reagent complex (e.g., Fe^{3+} - SCN^- [22], Hg^+ -diphenylcarbazide [21]); (ii) monitoring the concentration of an inert tracer added in proportion to PA by potentiometry or spectrophotometry (e.g., Li^+ , K^+ , Br^- , I^- , transition metal ion, dye) [23–25]; (iii) monitoring the intensity of fluorescence emitted from a tag covalently bound to PA [26, 27], and (iv) monitoring a change in spectroscopic characteristic on the interaction of PA with a metachromic or fluorochromic dye or a change in turbidity on the interaction of PA with a cationic surfactant [28–31]. Each of the abovementioned approaches has both advantages and the drawbacks. Indeed, the light absorption of PA complexes can be masked by the corrosion byproducts (formation of iron and copper complexes), by water background cation (iron, calcium, magnesium, copper) complexes formation, as well as by calcium carbonate and calcium sulfate colloid formation. At the same time, the indifferent markers do not guarantee the correct

PA concentration indication. Due to the differences in chemical properties of PA and a marker, the latter could have a different sorption ability relative to PA in a particular system. Therefore, the marker can provide either overestimation or an underestimation of PA content with a sequence of time. The PA-tagged fluorescent markers are treated as more reliable, although the more expensive solution [6]. Besides there is a risk of the PA antiscaling ability change due to the fluorescent fragment implementation. Thus, the chemical behavior of PA and of a corresponding PA-tagged fluorophore would be somehow different.

Recently, all the publications on the covalent binding of a fluorophore fragment to the anti-scalant molecule are restricted by either the polyacrylate or polyaspartate moieties [6–8, 13, 32–36]. Any reports on the fluorescent-tagged phosphonate-based antiscalants are missing, although the online phosphonate monitoring is no less actual.

2.1. Inert tracers added to polymeric antiscalants

Irrespective of a broad spectrum of the commercially available fluorescent dyes, the number of reagents that have a high quantum yield in an aqueous medium is relatively small [37]. It should be noted that the fluorescence intensity strongly depends on pH, background cation concentration, and bioimpurities, normally present in the circulating systems. Besides, some dyes may change the color of industrial water. Therefore, it is desirable to use those reagents that have maximal light absorption in the ultraviolet spectral range, while the emission spectrum is likely to correspond to the visible blue light.

Usually the fluorescent marker molecules combine sulfo-1,8-naphtalimide with some carboxylate or sulfo-groups to provide an aqueous solubility (fluorescein, rhodamine, sodium 1,3,6,8-pyrene-tetrasulfate) [38–40]. These reagents have high quantum yield, chemical, and photostability

Dye formula	Absorption maximum in H ₂ O, nm	Fluorescence maximum in H ₂ O, nm	Quantum yield, %
<p>Fluorescein</p>	473 (Buffer pH 5.0); 490 (Buffer pH 9.0)	514 (Buffers pH 5.0, pH 9.0)	92
<p>1,3,6,8-pyrene tetrasulfonic acid tetrasodium salt</p>	374	403	56

Table 1. The excitation and emission properties of fluorescein and of 1,3,6,8-pyrene tetrasulfonic acid tetrasodium salt [11, 41].

[11, 41] as shown in **Table 1**. Besides, Kurita Water Industries Ltd. offers a 2-phenylbenzimidazole as a marker [42], while Kemira Oyj proposes a lanthanoid-based tracer [43].

2.2. Fluorescent-tagged scale inhibitors

An antiscaling ability of fluorophore-tagged polymers relative to their non-tagged analogues was reported in a very few studies [6, 44–46], as shown in **Table 2**. Usually the implementation of a fluorophore fragment either does not change the inhibitor efficacy or even provides some enhancement.

Fluorescent-tagged scale inhibitors *	Concentration scale inhibitors, mg·dm ⁻³	Inhibitor efficacy, %	Reference
CaCO₃ scale			
PA-F1	10	49 ± 3	[6]
PA-F2	10	51 ± 2	[6]
MA-AA-F1	10	44 ± 2	[6]
MA-AA-F2	10	54 ± 2	[6]
PA	10	70 ± 2	[6]
FPASP	6	90	[44]
PASP	6	70	[44]
CaSO₄ scale			
PA-F1	10	73 ± 3	[6]
PA-F2	10	78 ± 2	[6]
MA-AA-F1	10	61 ± 2	[6]
MA-AA-F2	10	65 ± 2	[6]
PA	10	58 ± 2	[6]
AA-APEM-APTA	9	96	[45]
AA-APEM	9	95	[45]
PAA	9	85	[45]
Ca₃(PO₄)₂ scale			
FPASP	12	95	[46]
PASP	12	30	[46]

PA-F1: co-polymer acrylic acid–N-allyl-4-methoxy-1,8-naphtalimide. **PA-F2:** co-polymer acrylic acid–N-allyl-2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzamide (N-allylamidefluorescein). **MA-AA-F1:** co-polymer acrylic acid–fumaric acids–N-allyl-4-methoxy-1,8-naphtalimide. **MA-AA-F2:** co-polymer acrylic acid–fumaric acids–N-allyl-2-(6-hydroxy-3-oxo-3H-xanthen-9-yl)benzamide (N-allylamidefluorescein). **PA:** Na-salt of polyacrylic acid (Shandong TaiHe Water Treatment Co.Ltd.). **FPASP:** fluorescent polyaspartic acid was synthesized with partially ethanolamine-modified polysuccinimide, p-toluenesulfonyl chloride and 3-amino-9-ethyl carbazole. **AA-APEM-APTA:** co-polymer acrylic acid–oxalic acid–allylpolyethoxy carboxylate–8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (pyranine). **AA-APEM:** co-polymer acrylic acid–oxalic acid–allylpolyethoxy carboxylate. **PAA:** poly(acrylic acid), MW 1800 Da.

Table 2. An antiscaling ability of fluorophore-tagged polymers relative to their non-tagged analogues.

Inhibitor, 10 mg·dm ⁻³	Cation									
	Ca ²⁺		Mg ²⁺		Zn ²⁺		Cu ²⁺		Fe ³⁺	
	Cation concentration, mg·dm ⁻³									
	20	200	10	100	2	20	0.5	5	0.3	3
Fluorescence intensity change relative to the cation-free solution, %										
PA-F1	100 ± 1	93 ± 1	100 ± 1	100 ± 1	97 ± 1	96 ± 1	91 ± 1	74 ± 1	99 ± 1	94 ± 1
PA-F2	58 ± 1	43 ± 1	66 ± 1	62 ± 1	85 ± 1	42 ± 1	96 ± 1	48 ± 1	108 ± 1	94 ± 1
MA-AA-F1	81 ± 1	71 ± 1	91 ± 1	84 ± 1	93 ± 1	85 ± 1	90 ± 1	74 ± 1	94 ± 1	62 ± 1
MA-AA-F2	87 ± 1	81 ± 1	100 ± 1	138 ± 1	93 ± 1	90 ± 1	88 ± 1	69 ± 1	92 ± 1	60 ± 1

Table 3. The dependence of inhibitor fluorescence intensity on inorganic cation concentration (pH 8.0, 25°C) [6].

However some more experimental work has to be done in this field to make the situation clear.

Only a single paper reports on the influence of the background cations on the quantum yield of an antisclant [6], as shown in **Table 3**. The corresponding data clearly indicate that cations can either increase or sufficiently diminish the fluorescence intensity of some reagents, while some others stay insensitive to this influence. Anyhow this property has to be taken into account for any particular application of a tracer.

A covalent implementation of the fluorescent fragment into the polymer moiety can be performed in two ways. The first one assumes an attachment along with the polymer formation process. Another one is based on the fluorophore binding to the readymade polymer matrix. The first approach is used for the radical involved synthesis of co-polymers bearing carboxylate, sulfonic, or polyalkylenoxyde groups (acrylic, methacrylic, or maleic acids) and the dyes with an active double bond. The reaction runs in an aqueous solution being initiated by persulfates, by H₂O₂, benzoylperoxide, or by 2,2'-azobisisobutyronitrile (0.1–1.0%, mass). Also, such molecular mass regulators as sulfur compounds [47] or sodium hypophosphite are used [48]. These regulators keep the molecular masses within 2000–200,000 Da. The low molecular mass Mw of a polymer (1000 Da < Mw < 10,000 Da) is known to provide the most effective scale inhibition.

Generally, the fluorescent markers should meet the following requirements: (i) synthetic availability of the dyes capable for polymerization; (ii) a dye chemical stability during polymerization; (iii) a minimal influence of a dye on the polymer structure and on its Mw; (iv) the polymer structure, which should not affect the optical properties of a marker.

Fluorescent monomers used for a scale inhibitor implementation could be classified into three main categories: (i) aromatic hydrocarbons and their derivatives, for example, polyphenilic hydrocarbons, hydrocarbons with aryethylene or arylacetylene groups, and so on; (ii) heterocyclic monomers; and (iii) monomers with a carbonyl group.

Polyphenylhydrocarbons demonstrate an intensive fluorescence within a violet-to-blue visible spectrum region. Among these there are vinylanthracene (Rhodia Operations) [49], potassium

Figure 1. 9-vinyl anthracene (a), 2-allyldibenzosuberanol (b), and 8-(allyloxy)-1,3,6-pyrene trisulfonic acid (c) chemical structures.

2-alkyloxonaphtyl-6,8-disulfonate (China National Offshore Oil Corp.) [50], 2-allyldibenzosuberanol, and 9-allyl-9-hydroxyanthrene (Kurita Water Industries Ltd.) [51], as shown in **Figure 1**.

Numerous research groups synthesize a marker monomer via the 8-hydroxypyrene-1,3,6-trisulfonic acid (pyranine) interaction with allylchloride (**Figure 1c**) [52, 53]. Such a monomer reveals an intensive fluorescence with a maximum at 431 nm. Quantum yield is high. It depends on pH and varies within 80–90%. Then, these fluorescent monomers are co-polymerized (radical polymerization) with an antisclant-forming monomers, for example, acrylic acid and so on. (**Scheme 1**) [8].

Scheme 1. Preparation of co-polymer acrylic acid-oxalic acid-allylpolyethoxy carboxylate-8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt.

A co-polymerization of the pyranine-based monomers with maleic anhydride is also possible [35, 53–56]. The fluorescence intensity of an antiscalant correlates well with the fluorophore content in the scale inhibitor ($R \sim 0.99$), while the detection limit ranges from 1 to 2 $\text{mg} \cdot \text{dm}^{-3}$ [35, 53–56]. Among the numerous water treatment reagents developed by Nalco Chemical Co. there are two fluorescent monomers of the pyranine group [57], as shown in **Figure 2**.

Besides antiscalants, these monomers can also be implemented into some biocides. However, the Nalco Chemical Co. also uses some inert tracers along with the polymer-tagged ones.

Another important group of fluorophore monomers is represented by 5- and 6-member heterocycles [44, 49], particularly by a vinylimidazolic monomer [58], as shown in **Figure 3**.

Among the fluorophores with a carbonyl group, it is reasonable to mention an inhibitor with a fluorescence fragment dimethyl-(4-(7-methoxycoumarin))-methyl-(acryloyloxy)-ethyl-ammonium bromide [59], as shown in **Figure 4**. It reveals the maximal fluorescence intensity at 390 nm.

Several publications report on the naphthalic acid-based markers for biochemical analysis application [60, 61]. An interest in these reagents is associated with both synthetic availability of some valuable 1,8-naphthalimide derivatives and with promising optical properties [62–64]. Ecolab Inc. (USA) has proposed fluorescent monomers derived from 3,4-7H-benzo[d,e]anthracenedicarboxylic acid for the antiscalant labeling [65]. Among these N-(3-N',N'-Dimethylaminopropyl)benzo(k,l)xanthene-3,4-dicarboxylic imide of 2-hydroxy-3-allyloxy-propyl quaternary salt seems to be the most interesting, as shown in **Figure 5**.

A considerable attention is paid to the 1,8-naphthalimide derivatives in relevance to the desalination processes (reverse osmosis) [66–68], as shown in **Figures 6 and 7**.

Figure 2. Nalco fluorophores for a covalent attachment to the scale inhibitors [57]; $M = \text{H}^+, \text{NH}_4^+, \text{K}^+, \text{Na}^+, \text{Cs}^+, \text{Rb}^+, \text{Li}^+$; $n = 1, 2, 3, 4, 6$ or 9 .

Figure 3. Vinylimidazolic monomer structure; R, R^1 , and R^2 are denoted as H , alkyl, aryl, phosphate, nitrate, or sulfate groups.

Figure 4. An antiscalant with a dimethyl-(4-(7-methoxycoumarin))-methyl-(acryloyloxy)-ethyl-ammonium bromide fragment [59].

Figure 5. N-(3-N',N'-Dimethylaminopropyl)benzo(k,l)xanthene-3,4-dicarboxylic imide of 2-hydroxy-3-allyloxypropyl quaternary salt [65].

Figure 6. Some 1,8-naphthalimide-tagged antiscalants [66, 67].

An implementation of a fluorophore into a PASP molecule is normally performed not via copolymerization but by its attachment to the already formed polymer molecule [46, 69, 70]. Some authors propose 3-amino-9-ethylcarbazole [71] or N-(2,3-epoxypropyl)carbazole [72] for the PASP molecule labeling, as shown in **Figure 8**.

Figure 7. Some 1,8-naphthalimide-based fluorophore monomers developed by Nalco for antiscalant labeling [68].

Figure 8. 3-amino-9-ethylcarbazole (a) and N-(2,3-epoxypropyl)carbazole (b) fluorophore structures.

A special attention has to be paid to the communication, where a fluorescence of the inhibitor itself (carboxymethyl ammonium oligochitosan) is reported [73]. This antiscalant does not need any fluorescent marker attachment. The corresponding synthetic method is presented in **Scheme 2**.

It was found that the fluorescence intensity increases under acidic conditions. Thus, the hydrogen bonding and the electrostatic repulsion provide a rigid and densely stabilized structure formation, which is necessary for inducing fluorescence. Hence, the fluorescence of carboxymethyl quaternary ammonium oligochitosan may have been caused by the effect of the $n \rightarrow \pi^*$ transition between $-C=O-$ and $-NH-$ and the special rigid structure formed by hydrogen bonding and a charge-charge repulsion [73]. The fluorescence maximum corresponds to 460 nm, while the detection limit at pH 5–9 is within $0.61 \text{ mg} \cdot \text{dm}^{-3}$.

Scheme 2. Carboxymethyl quaternary ammonium oligochitosan synthesis.

2.3. Visualization of scale inhibition mechanisms

Irrespective of the broad, successful, and long-term antiscalant applications, the mechanisms of scale inhibition still appear in the matter of discussions [14, 74–81]. In this sense, the fluorophore-tagged antiscalants can provide the unique and amazing opportunities to get a deep insight of the scale inhibition mechanisms. As far as we know, recently, such reports on the scale inhibition visualization are missing. However, our research group managed to synthesize a conjugate of 1,8-naphthalimide and HEDP: 1-hydroxy-7-(6-methoxy-1,3-dioxo-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)heptane-1,1-diyl-di(phosphonic acid), (HEDP-F), as shown in **Figure 9a**. This reagent was tested as an antiscalant in gypsum scale formation experiments performed according to NACE protocol [82]. According to this protocol, a calcium-containing brine and a sulfate-containing brine are mixed to form a supersaturated gypsum aqueous solution in the presence of 0.5–15 mg·dm⁻³ of an inhibitor at ambient temperature. Then, this solution is kept for 24 h at 71°C, cooled, and analyzed for residual calcium content by EDTA titration. In a parallel run, the gypsum crystals have been isolated and analyzed with a fluorescence scanning microscope, as shown in **Figure 9b**.

Unlike the scanning electron microscopy, the fluorescence provides a unique possibility to look inside the crystal. Therefore, all the steps of crystal formation become visible. One can see that the bright crystal rod (“lightsaber”), initially formed by nanoparticles, is completely covered with HEDP-F. Then, this rod becomes the center of gypsum layers’ growth without any resistance or involvement of a HEDP-F antiscalant (massive dark layer). Finally, after the gypsum crystal formation is finished, the residual HEDP-F molecules get adsorbed on its surface, particularly at the edges of a crystal lattice, forming the outer layer. This is indicated by green spots and stripes¹. Evidently,

Figure 9. HEDP-F (a) and an image of a Gypsum crystal, isolated in presence of HEDP-F (b); laser scanning microscope LSM-710 Carl Zeiss, lambda mode with 458 nm excitation; 26.10.2017. Data presented by Semen Kamagurov, Sergey Tkachenko and Maxim Oshchepkov.

¹A full-scale publication is under in preparation

these data reveal a mechanism, significantly different from the conventional ones [74–81]. By all means the visualization of scale inhibition mechanisms by fluorescent-tagged antiscalants seems to become a very promising tool of the scale inhibition theory development.

Besides, these reagents can provide some unique opportunities for reverse osmosis membrane mapping, scale inhibition traceability in the pipes, and a scale inhibitor localization in a circulation water facility.

3. Gaseous oxygen monitoring in wastewater

Biological treatment of wastewater includes activated sludge aeration. This in turn raises a problem of the gaseous oxygen content monitoring. One of the most promising solutions here is the fiber-optic oxygen sensor application. This method is based on the ability of oxygen molecules to suppress the luminescence of some luminophores [10, 83]. A fruitful application of some pyrene- or decacylene-based fluorophores along with some ruthenium complex is reported: $(\text{Ru}(\text{bpy})_3)^+$, $\text{Ru}(\text{phen})_3^+$, $[\text{Ru}(\text{dpp})_2\text{Phen}]^{2+}$ (dpp = 4, 7-diphenyl-1,10-phenanthroline, Phen = 1,10-phenanthroline) [84], as shown in **Figure 10**. Also some terbium(III) complexes have been immobilized

Figure 10. Structure of $[\text{Ru}(\text{dpp})_2\text{Phen}]^{2+}$.

Figure 11. Structure of $\text{Tb}(\text{acac})_3\text{phen}$.

on aluminum oxide ($\text{Tb}(\text{acac})_3\text{phen}$), where acac-acetylacetone [85], as shown in **Figure 11**, as well as some porphyrin complexes of Pt and Pd [86], is worth mentioning.

The emitted blue light (~ 475 nm) of a photogenerator excites the fluorescence of a specially selected chemical complex, placed at the end of a fiber-optic oxygen sensor (sol-gel matrix). The excited complex generates fluorescence with a wavelength which is around 600 nm. This fluorescence gets suppressed by the oxygen present in a sample [87–89]. This provides an effective oxygen concentration measurement in water within the range from 0 to 40.7 ppm [90].

4. Fluorescent total ATP count in wastewaters

The total bacterial count in wastewater is based on bioluminescence. Normally it is used for the industrial and wastewater quality assessment, while for the drinking water it is not so common. The method is known since 1947, when McElroy has demonstrated that bioluminescence of a glowworm is closely associated with adenosine triphosphate (ATP) content [91]. Thus, the measurement of ATP provides an efficient indication of bacterial pollution of water according to **Scheme 3** [12]:

Analysis involves the firefly luciferase-luciferin system. Its contact with ATP molecules generates the “cold” light, counted by a luminometer within 15–20 s. The sensitivity of analysis is very high. It provides detection of 10^{-17} ATP moles per liter. Recently, there have been some standard solutions for luminometers present at the market: EnSURE™, SystemSURE Plus™ Clean Trace™, NovaLum™, Firefly 2™, Accupoint™, russian-made LYUM-1, Lumitester PD-20™ etc. [92].

Scheme 3. Bioluminescent reaction catalyzed by firefly luciferase.

5. Other applications

Some water treatment facilities require the oil component control in wastewater [9, 93]. Organic pollutants can occur in the cooling water, in the technical-use water, in a boiler-feeding water, and due to the leaks of oils into the steam condensate. For online pollutants' monitoring, the fluorescent sensors are broadly used. The method is highly sensitive. Depending on the type of oil, the detection limits may vary from 1 to 100 ppm. Most of the oils contain some polycyclic aromatic hydrocarbons (PAHs) [94], capable of generating blue or violet fluorescence being exposed to UV irradiation. Usually the excitation light wavelength corresponds to 254 nm, while the detection operates in a 360 nm spectrum range.

Finally, one of the first known applications of fluorophores in water treatment should be mentioned. It is associated with water leaks detection in industrial pipelines. To solve this problem, some fluorescent indicators, for example fluorescein, have been merely added to the circulating water [11].

6. Conclusions

The fluorescent markers added to the circulating water or wastewaters find a broad spectrum of analytical applications for online quality monitoring. The most promising and a fast-developing field is a scale inhibitor concentration detection via antiscalant-tagged reagents. At the same time the visualization of scale inhibition mechanisms by the fluorescent-tagged antiscalants is a very promising tool of the scale inhibition theory development. Besides, these reagents can provide some unique opportunities for reverse osmosis membrane mapping, scale inhibition traceability, and a scale inhibitor localization in a circulation water facility.

Acknowledgements

The authors would like to thank the Russian Foundation for Basic Research (Project No. 17-08-00061).

Conflict of interest

For the present study, no economic interest or any conflict of interest exists.

Author details

Maxim Oshchepkov^{1,2} and Konstantin Popov^{2*}

*Address all correspondence to: ki-popov@mtu-net.ru

1 Mendelev University of Chemical Technology of Russia, Moscow, Russian Federation

2 PJSC "Fine Chemicals R&D Centre", Moscow, Russian Federation

References

- [1] Duval R, Duplais C. Fluorescent natural products as probes and tracers in biology. *Natural Product Reports*. 2017;**34**:161-193. DOI: 10.1039/C6NP00111D

- [2] Drummen GPC. Fluorescent probes and fluorescence (microscopy) techniques – Illuminating biological and biomedical research. *Molecules*. 2012;**17**:14067-14090. DOI: 10.3390/molecules171214067
- [3] Lange J, Olsson O, Sweeney B, Herbstritt B, Reich M, Alvarez-Zaldivar P, Payraudeau S, Imfeld G. Fluorescent tracers to evaluate pesticide dissipation and transformation in agricultural soils. *Science of the Total Environment*. 2018;**619-620**:1682-1689. DOI: 10.1016/j.scitotenv.2017.10.132
- [4] Arenas-Vivo A, Beltran FR, Alcazar V, de la Orden MU, Martinez UJ. Fluorescence labeling of high density polyethylene for identification and separation of selected containers in plastics waste streams. Comparison of thermal and photochemical stability of different fluorescent tracers. *Materials Today Communications*. 2017;**12**:125-132. DOI: 10.1016/j.mtcomm.2017.07.008
- [5] Jiangli F, Suzhen W, Wen S, Shigang G, Yao K, Jianjun D, Xiaojun P. Anticancer drug delivery systems based on inorganic nanocarriers with fluorescent tracers. *American Institute of Chemical Engineers Journal Ahead of Print*. 2017. DOI: 10.1002/aic.15976
- [6] Popov K, Oshchepkov M, Kamagurov S, Tkachenko S, Dikareva Y, Rudakova G. Synthesis and properties of novel fluorescent-tagged polyacrylate-based scale inhibitors. *Journal of Applied Polymer Science*. 2017;**134**:45017. DOI: 10.1002/APP.45017
- [7] Zhenling S, Xin Z, Puyu Z. Preparation of fluorescent polyaspartic acid and evaluation of its scale inhibition for CaCO_3 and CaSO_4 . *Polymers for Advanced Technologies*. 2017;**28**:367-372. DOI: 10.1002/pat.3897
- [8] Guangqing L, Xue M, Yuming Z. Fluorescent-tagged block copolymer as an effective and green inhibitor for calcium sulfate scales. *Russian Journal of Applied Chemistry*. 2016;**89**:1861-1868. DOI: 10.1134/S1070427216110185
- [9] Ruhala SS, Zarnetske JP. Using in-situ optical sensors to study dissolved organic carbon dynamics of streams and watersheds: A review. *Science of the Total Environment*. 2017;**575**:713-723. DOI: 10.1016/j.scitotenv.2016.09.113
- [10] Allen CB, Schneider BK, White CJ. Limitations to oxygen diffusion in in vitro cell exposure systems in hyperoxia and hypoxia J. *American Journal of Physiology-Lung Cellular and Molecular Physiology*. 2001;**281**:L1021-L1027. DOI: 10.1152/ajplung.2001.281.4.L1021
- [11] Sabnis RW. *Handbook of Fluorescent Dyes and Probes*. 1st ed. Hoboken, NJ, USA: John Wiley & Sons, Inc; 2015. DOI: 10.1002/9781119007104
- [12] Guardigli M, Lundin A, Roda A. “Classical” applications of Chemiluminescence and bioluminescence. In: Roda A, editor. *Chemiluminescence and Bioluminescence: Past, Present and Future*. Royal Society of Chemistry; 2010. pp. 143-190. DOI: 10.1039/9781849732024-00141
- [13] Jiao CL, Wu YF, Hou CY, Cheng GC, Wu DX, Xu X, Yin JH. Determine the consumption of fluorescent scale inhibitor SC260 using Dibenzofuran-2-sulfonic acid hydrate. *Advanced Materials Research*. 2014;**997**:247-250. DOI: 10.4028/www.scientific.net/AMR.997.247

- [14] Popov KI, Oshchepkov MS, Shabanova NA, Dikareva YM, Larchenko VE, Koltinova EY. DLS study of a phosphonate induced gypsum scale inhibition mechanism using indifferent nanodispersions as the standards of a light scattering intensity comparison. *International Journal of Corrosion and Scale Inhibition*. 2018;**7**:9-24. DOI: 10.17675/2305-6894-2018-7-1-2
- [15] Amjad Z, editor. *The Science and Technology of Industrial Water Treatment*. Boca Raton Florida: CRS Press; 2010. p. 530
- [16] MacAdam J, Parsons SA. Calcium carbonate scale formation and control. *Reviews in Environmental Science and Biotechnology*. 2004;**3**:159-169. DOI: 10.1007/s11157-004-3849-1
- [17] Popov KI, Kovaleva NE, Rudakova GY, Kombarova SP, Larchenko VE. Recent state-of-the-art of biodegradable scale inhibitors for cooling water treatment applications (review). *Thermal Engineering*. 2016;**63**:122-129. DOI: 10.1134/S0040601516010092
- [18] Hasson D, Shemer H, Sher A. State of the art of friendly “green” scale inhibitors: A review article. *Industrial and Engineering Chemistry Research*. 2011;**50**:7601-7607. DOI: 10.1021/ie200370v
- [19] Popov K, Rudakova G, Larchenko V, Tusheva M, Afanas’eva E, Kombarova S, Kamagurov S, Kovaleva N. A comparative performance ranking of some phosphonates and environmentally friendly polymers on CaCO_3 scaling inhibition by NACE protocol. *Desalination and Water Treatment*. 2017;**69**:163-172. DOI: 10.5004/dwt.2016.0336
- [20] Pervov A, Andrianov A, Rudakova G, Popov K. A comparative study of some novel “green” and traditional antiscalants efficiency for the reverse osmotic Black Sea water desalination. *Desalination and Water Treatment*. 2017;**73**:11-21. DOI: 10.5004/dwt.2017.20363
- [21] Yuchi A, Gotoh Y, Itoh S. Potentiometry of effective concentration of polyacrylate as scale inhibitor. *Analytica Chimica Acta*. 2007;**594**:199-203. DOI: 10.1016/j.aca.2007.05.049
- [22] Glukhova LY, Perov PA. Spectrophotometric method for the determination of an acrylic acid-acrylamide copolymer in highly mineralized waters. *Khimiya i Tekhnologiya Vody. Soviet Journal of Water Chemistry and Technology*. 1981;**3**:236-237. ISSN: 0204-3556
- [23] Hoots JE, Hunt BE. Monitoring chemical treatment with fluorescent tracers. U.S. Patent. US4783314 A 19881108; 1988
- [24] Hoots JE, Banks RH, Johnson DA. Transition metals as chemical tracers in aqueous systems. U.S. Patent. US4966711 A 19890227; 1990
- [25] Yoshimura S, Kuzumaki S, Imahama T. Method for controlling concentration of chemicals added to industrial water. JPN Patent. JP2788354B2; 1991
- [26] Myers RR, Fink JE. Method for the colorimetric determination of polycarboxylates in aqueous systems. U.S. Patent. US4894346A; 1990
- [27] Hoots JE, Pierce CC, Kugel RW. Monitoring and in-system concentration control of poly-electrolytes in waters using fluorochromatic dyes. U.S. Patent. US5389548A; 1995

- [28] Ma J, Sun Y, Yu Z. High-efficiency phosphorus-free corrosion and scale inhibition dispersion agent, preparation method thereof and application thereof. PRC Patent. CN102139967B; 2012
- [29] Tong Z, Chu C, Fan E, Sha Z. High-efficiency low-phosphorus corrosion and scale inhibiting dispersant and its preparation method. PRC Patent. CN102745825A; 2012
- [30] Fong DW, Hoots JE. Fluorescent group-tagged acrylic polymers and their synthesis by post-polymerization (trans)amidation. U.S. Patent. US5128419; 1992
- [31] Kira M, Kobayashi N. Agent for water treatment containing a polymer for water treatment and a process for producing said polymer. U.S. Patent. US5635575; 1997
- [32] Hoots J, Burkart C, Paulson S. Tracing process problems. *Chemical Engineering Progress*. 2002;**98**:66-70
- [33] Zeiner KEH, Ho B, Williams KD. Novel antiscalant dosing control. *Desalination*. 2003;**157**:209-216. DOI: 10.1016/S0011-9164(03)00400-4
- [34] Vazques O, Mackay E, Tjomsland T, Nygard O, Storås E. Use of tracers to evaluate and optimize scale squeeze treatment design in the Norne field. *SPE Production and Operations*. 2014;**29**:5-13. DOI: 10.2118/164114-PA
- [35] Wu K, Chen F, Liu Y, Luo J. Preparation and properties of β -cyclodextrins polymer used as calcium carbonate scale inhibitor containing fluorescent groups. *Research on Chemical Intermediates*. 2014;**41**:7617-7630. DOI: 10.1007/s11164-014-1847-7
- [36] Wang J, Peng Y, Guo W, Ji R, Zhao L, Jia Y, Gao C. Characterization of Tinopal CBS-X as a fluorescent tracer in cooling water. *Instrumentation Science and Technology*. 2016;**45**:301-311. DOI: 10.1080/10739149.2016.1237367
- [37] Lakowitz JR. *Principles of Fluorescence Spectroscopy*. 3rd ed. New York: Springer; 2006
- [38] Feng H, Luo R, Shang W, Zhang L, Zhang W. Phosphorus-free corrosion and scale inhibitor. PRC Patent. CN101767885B; 2011
- [39] Ito M, Ichikawa S, Kashimura H. Method For Stabilizing Fluorescence Intensity Of Rhodamine-Based Fluorescent Material. JPN Patent. JP5297851B2; 2013
- [40] Xu Guangming, Chen Jun, Lv Zhen, Chen Bo, He Gongzhe, Shi Yadong, Zhang Feiyan, Zhu Di, Guan Yuntao, He Kai. Scale and corrosion inhibitor. PRC Patent. CN103319010A; 2013
- [41] Tran-Thi T-H, Prayer C, Millie P, Uznanski P, Hynes JT. Substituent and solvent effects on the nature of the transitions of pyrenol and pyranine. Identification of an intermediate in the excited-state proton-transfer reaction. *The Journal of Physical Chemistry*. 2002;**106**:2244-2255. DOI: 10.1021/jp0125606
- [42] Hajime I, Mayumi K, Kanji N. Concentration control method for water-based additive. Jpn patent. JPH09178662A; 1997

- [43] Nuutinen V, Toivonen S, Johnstone J, Harma H, Lehmusto M, Tiittanen S, Vaisanen P, Siivonen J, Mundill P. Method for analyzing a sample comprising at least a first and a second oil field scale inhibitor. (2015). PCT Int. Appl. WO2015075309A1
- [44] Kamagurov SD, Kovaleva NE, Oshchepkov MS, Popov KI, Tkachenko SV, Starkova ES. Fluorophor and method for obtaining salt inhibitor containing fluorophor as fluorescent mark. Russ. Patent. RU 2640339 C2 20171227; 2017
- [45] Wang H, Zhou Y, Yao Q, Sun W. Calcium sulfate precipitation studies with fluorescent-tagged scale inhibitor for cooling water systems. *Polymer Bulletin*. 2015;**72**:2171-2188. DOI: 10.1007/s00289-015-1396-2
- [46] Feng J, Gao L, Wen R, Deng Y, Wu X, Deng S. Fluorescent polyaspartic acid with an enhanced inhibition performance against calcium phosphate. *Desalination*. 2014;**345**:72-76. DOI: 10.1016/j.desal.2014.04.019
- [47] Detering J, Urtel B, Weber H, Ettl R, Gaedt T, Heintz E, Bastigkeit T, Eiting T, Sendor-Mueller D. Copolymers containing carboxylic acid groups, sulphonic acid groups and polyalkylene oxide groups as anti-scaling additive to washing and cleaning agents. Russ. Patent RU2574395; 2016
- [48] Detering J, Urtel B, Nied S, Heintz E. Low-Molecular, Phosphorus-containing polyacrylic acids and use thereof as scale inhibitors in water supply systems. Russ. Patent. RU2593591C2; 2016
- [49] Hills E, Touzet S, Langlois B. Stimulating Oilfields Using Different Scale-Inhibitors. U.S. Patent. US7703516B2; 2007
- [50] Shuzhong H, Weisheng Z, Yu R, Houkai T, Xiangyan M, Longxin Y, Wu X, Wang J. Preparation method of acrylic polymer with fluorescence characteristic. PRC Patent. CN103242476B; 2015
- [51] Mayumi K, Norimasa K. Agent for water treatment containing a polymer for water treatment and a process for producing said polymer. U.S. Patent (1997). US5635575A
- [52] Liu G, Huang J, Zhou Y, Yao Q, Wang H, Ling L, Zhang P, Ke C, Liu Y, Wendao W, Sun W. Carboxylate-terminated double-hydrophilic block copolymer containing fluorescent groups: An effective and environmentally friendly inhibitor for calcium carbonate scales. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 2013;**62**:678-685. DOI: 10.1080/00914037.2013.769226
- [53] Kun D, Zhou Y, Dai L, Wang Y. Preparation and properties of polyether scale inhibitor containing fluorescent groups. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 2008;**57**:785-796. DOI: 10.1080/00914030801962988
- [54] Kun D, Zhou Y, Wang L, Wang Y. Fluorescent-tagged no phosphate and nitrogen free calcium phosphate scale inhibitor for cooling water systems. *Journal of Applied Polymer Science*. 2009;**113**:1966-1974. DOI: 10.1002/app.30213

- [55] Huang G, Zhou J, Yao Y, Ling Q, Zhang L, Wang P, Cao H, Liu K, Wu Y, Sun W, Hu W, Zhengjun. Fluorescent-tagged double-hydrophilic block copolymer as a green inhibitor for calcium carbonate scales. *Tenside Surfactants Detergents*. 2012;**49**:404-412. DOI: 10.3139/113.110210
- [56] Wang H, Zhou Y, Yao Q, Ma S, Wendao W, Sun W. Synthesis of fluorescent-tagged scale inhibitor and evaluation of its calcium carbonate precipitation performance. *Desalination*. 2014;**340**:1-10. DOI: 10.1016/j.desal.2014.02.015
- [57] Moriarty Barbara E, Wei Mingli, Hoots John E, Workman David P, Rasimas Jeffrey P. Fluorescent monomers and polymers containing same for use in industrial water systems. U.S. Patent (2001). US6312644B1
- [58] Moore L, Clapp L. Tagged scale inhibitor compositions and methods of inhibiting scale. U.S. Patent. US8980123B2;2015
- [59] Ying W, Peng L, Jiajun F, Xiaodong L, Zhuo L, Xuelong L. Fluorescence-trace water processing agent containing coumarins derivative groups and preparation method thereof. PRC Patent. CN103482777B; 2015
- [60] Mittapalli RR, Namashivaya SSR, Oshchepkov AS, Kuczyńska E, Kataev EA. Design of anion-selective PET probes based on azacryptands: The effect of pH on binding and fluorescence properties. *Chemical Communications*. 2017;**53**:4822-4825. DOI: 10.1039/C7CC01255A
- [61] Oshchepkov AS, Mittapalli RR, Fedorova OA, Kataev EA. Naphthalimide-based polyammonium chemosensors for anions: Study of binding properties and sensing mechanisms. *Chemistry - A European Journal*. 2017;**23**:9657-9665. DOI: 10.1002/chem.201701515
- [62] Oshchepkov AS, Oshchepkov MS, Arkhipova AN, Panchenko PA, Fedorova OA. Synthesis of 4-nitro-N-phenyl-1,8-naphthalimide annulated to thia- and azacrown ether moieties. *Synthesis-Stuttgart*. 2017;**49**:2231-2240. DOI: 10.1055/s-0036-1588712
- [63] Oshchepkova MV, Oshchepkov MS, Fedorova OA, Fedorov YV, Lozinskii VI. New copolymer gels based on N,N-dimethylacrylamide and crown-containing allyl derivative of 1,8-naphthalimide as optical sensors for metal cations in an organic medium. *Doklady Physical Chemistry*. 2017;**476**:181-185. DOI: 10.1134/S0012501617100050
- [64] Oshchepkova MV, Oshchepkov AS, Zaborina OE, Fedorova OA, Fedorov YV, Lozinsky VI. Fluorescent cryogels based on copolymers of N,N-dimethylacrylamide and allyl derivatives of 1,8-naphthalimide. *Polymer Science Series B*. 2015;**57**:631-637. DOI: 10.1134/S1560090415060159
- [65] Atkins JM, Moriarty BE, Zinn PJ. Fluorescent monomers and tagged treatment polymers containing same for use in industrial water systems. U.S. Patent. US2014183140A1; 2014
- [66] Zhang Y, Zhang Q, Shi Y, Lei W, Xia M, Wang F. Fluorescence labeling acrylic acid-sodium acrylic sulphonate co-polymer water treatment agent and preparation method thereof. PRC Patent. CN101381168B; 2010

- [67] Lei XM. Methoxy group naphthyl fluorescence marked water treating agent and its preparing method. PRC Patent. CN1781857A; 2006
- [68] Morris JD, Moriarty BE, Wei Mingli, Murray PG, Reddinger JL. Fluorescent Monomers and Tagged Treatment Polymers Containing Same for Use in Industrial Water Systems. 2001. PCT Int. Appl. WO 2001081654 A1 20011101
- [69] Zhang B, Zhou D, Lu X, Xu Y, Ciu Y. Synthesis of polyaspartic acid/3-amino-1H-1,2,4-triazole-5-carboxylic acid graft copolymer and evaluation of its corrosion inhibition and scale inhibition performance. *Desalination*. 2013;**327**:32-38. DOI: 10.1016/j.desal.2013.08.005
- [70] Xu Y, Zhang B, Zhao L, Ciu Y. Synthesis of polyaspartic acid/3-aminoorotic acid graft copolymer and evaluation of its scale inhibition and corrosion inhibition performance. *Desalination*. 2013;**311**:156-161. DOI: 10.1016/j.desal.2012.11.026
- [71] Gao L-J, Feng J-Y, Jin B, Zhang Q-N, Liu T-Q, Lun Y-Q, Wu Z-J. Carbazole and hydroxy groups-tagged poly(aspartic acid) scale inhibitor for cooling water system. *Chemistry Letters*. 2011;**40**:1392-1394. DOI: 10.1246/cl.2011.1392
- [72] Lijun G, Jiuying F. Fluorescent labeling polyaspartic acid scale inhibitor and preparation method thereof. PRC Patent. CN102910746B; 2013
- [73] Huixin Z, Zhiyue C, Xiuhong J, Dongxue S, Dongdong W, Tingru Y, Jie Z, Xu H. Preparation of modified oligochitosan and evaluation of its scale inhibition and fluorescence properties. *Journal of Applied Polymer Science*. 2015;**132**:42518. DOI: 10.1002/app.42518
- [74] Elliott MN. Scale control by threshold treatment. *Desalination*. 1970;**8**:221-236. DOI: 10.1016/S0011-9164(00)80231-3
- [75] Reddy MM, Nancollas GH. Calcite crystal growth inhibition by phosphonates. *Desalination*. 1973;**12**:61-73. DOI: 10.1016/S0011-9164(00)80175-7
- [76] Tomson BM, Fu G, Watson MA, Kan AT. Mechanisms of mineral scale inhibition. *SPE Production & Facilities*. 2003;**18**:192-199. DOI: 10.2118/84958-PA
- [77] GuiCai Z, JiJiang G, MingQin S, BinLin P, Tao M, ZhaoZheng S. Investigation of scale inhibition mechanisms based on the effect of scale inhibitor on calcium carbonate crystal forms. *Science in China, Series B Chemistry*. 2007;**50**:114-120. DOI: 10.1007/s11426-007-0010-3
- [78] Lixiu L, Aijiang H. Research progress of scale inhibition mechanism. *Advanced Materials Research*. 2014;**955-959**:2411-2414. DOI: 10.4028/5].scientific.net/AMR.955-959.2411
- [79] Al-Roomi YM, Hussain KF. Potential kinetic model for scaling and scale inhibition mechanism. *Desalination*. 2016;**393**:186-195. DOI: 10.1016/j.desal.2015.07.025
- [80] Ji-jiang G, Wang Y, Gui-cai Z, Jiang P, Mingqin S. Investigation of scale inhibition mechanis based on the effect of HEDP on surface charge of calcium carbonate. *Tenside, Surfactants, Detergents*. 2016;**53**:29-36. DOI: 10.3139/113.110407

- [81] Hoang TA. Mechanisms of scale formation and inhibition. In: Amjad Z, Demadis K, editors. *Mineral Scales and Deposits, Scientific and Technological Approaches*. 1st ed. Elsevier; 2015. pp. 47-83
- [82] NACE Standard TM0374-2007 (formerly TM0374-2001) Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution (for Oil and Gas Production Systems). Item No. 21208. 2007
- [83] Krihak M, Murtaugh MT, Shahriari MR. Fiber Optic Oxygen Sensors Based on the Sol-Gel Coating Technique. *Proc. SPIE-The International Society for Optical Engineering (Chemical, Biochemical and Environmental Fiber Sensors VIII)*. Vol. 2836/1996. pp. 105-115. DOI: 10.1117/12.260583
- [84] Lei B, Li B, Zhang H, Zhang L, Li W. Synthesis, characterization, and oxygen sensing properties of functionalized Mesoporous SBA-15 and MCM-41 with a covalently linked ruthenium(II) complex. *Journal of Physical Chemistry C*. 2007;**111**:11291-11301. DOI: 10.1021/jp070008w
- [85] Li S, Song H, Li W, Ren X, Lu S, Pan G, Fan L, Yu H, Zhang H, Qin R, Dai QL, Wang T. Improved photoluminescence properties of ternary terbium complexes in Mesoporous molecule sieves. *The Journal of Physical Chemistry. B*. 2006;**110**:23164-23169. DOI: 10.1021/jp064509d
- [86] Papkovskij DB, Ponomarev GV, Kurochkin IN, Chernov SF. Metal complexes of porphyrin-ketones, sensitive member for oxygen optical assay in liquid or gaseous medium and a method of oxygen determination. *Russ. Patent*. RU2064948C1; 1996
- [87] Krihak M, Shahriari MR. A highly sensitive, all solid state Fiber optic oxygen sensor based on the sol-gel coating technique. *Electronic Letters*. 1996;**32**:240-242. DOI: 10.1049/el:19960104
- [88] Shahriari MR, Murtaugh MT, Kwon HC. Ormosil Thin Films for Chemical Sensing Platforms. *Proc. SPIE-The International Society for Optical Engineering (Chemical, Biochemical and Environmental Fiber Sensors IX)*. Vol. 3105/1997. pp. 40-51. DOI: 10.1117/12.276133
- [89] Wang W, Reimers CE, Wainright SC, Shahriari MR, Morris MJ. Applying Fiber-optic sensors for monitoring dissolved oxygen. *Sea Technology*. 1999;**40**:69-74
- [90] Weiwei F, Na Z, Lingxin C, Bowei L. An optical sensor for monitoring of dissolved oxygen based on phase detection. *Journal of Optics*. 2013;**15**:055502/1-005502/7. DOI: 10.1088/2040-8978/15/5/055502
- [91] McElroy WD. The energy source for bioluminescence in an isolated system. *Proceedings of the National Academy of Sciences of the United States of America*. 1947;**33**:342-345. DOI: 10.1073/pnas.33.11.342

- [92] Björkman KM, Karl DM. A novel method for the measurement of dissolved adenosine and guanosine triphosphate in aquatic habitats: Applications to marine microbial ecology. *Journal of Microbiological Methods*. 2001;**47**:159-167. DOI: 10.1016/S0167-7012(01)00301-3
- [93] Han TN, Hao NH, Taro U, Yew-Hoong GK. A critical review on characterization strategies of organic matter for wastewater and water treatment processes. *Bioresource Technology*. 2015;**193**:523-533. DOI: 10.1016/j.biortech.2015.06.091
- [94] Carstea EM, Bridgeman J, Baker A, Reynolds DM. Fluorescence spectroscopy for wastewater monitoring: A review. *Water Research*. 2016;**95**:205-219. DOI: 10.1016/j.watres.2016.03.021